Picosecond Radical Kinetics. Fast Ring Openings of Secondary and Tertiary *trans*-2-Phenylcyclopropylcarbinyl Radicals

Seung-Yong Choi, Patrick H. Toy, and Martin Newcomb*

Department of Chemistry, Wayne State University, Detroit, Michigan, 48202

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Precursors to reactive intermediates that rearrange have been applied widely in mechanistic probe studies wherein one seeks to implicate a reactive intermediate by the detection of rearranged products. For such purposes, the rearrangement must be faster than competing reactions of the unrearranged intermediate, and very fast rearrangements often are desired. If the reactive intermediate in question is a radical and the rate constant for the radical rearrangement is known, the intermediate can be referred to as a "radical clock" which can be used to "time" competing radical processes.[1,2] Our interest in radical kinetics and in probe studies of biochemical processes that might involve radical intermediates led us to develop an indirect kinetic method, the PTOC-thiol or PTOC-selenol method, for measuring the kinetics of radicals that have lifetimes in the picosecond range at room temperature.[3−6] We have used this method for the calibration of several ring openings of phenyl-substituted cyclopropylcarbinyl radicals, **1a**−**3a**,[7] **4a** and **5a**,[8] and **6a**−**9a**[9] (Figure 1), which are among the fastest calibrated radical reactions.

The calibration of ultrafast 2-arylcyclopropylcarbinyl radical clocks has permitted quantitative applications of the corresponding hydrocarbon precursors in studies of enzyme-catalyzed hydroxylation reactions in an attempt to implicate radical intermediates and to time the "oxygen rebound" step in these processes. Probe **1b** has been used to study hydroxylation by a non-heme monooxygenase in cells of *Pseudomonas oleovorans*,[10] reconstituted soluble methane monooxygenase (sMMO) hydroxylase from *Methylococcus capsulatus* (Bath) and *Methylosinus trichosporium* OB3b,[11] chloroperoxidase (CPO) from *Caldariomyces fumago*,[12,13] and various cytochrome P450 (P450) enzymes.[14−16] Probes **3b**,[14] **5b**,[17] and **6b**[18] have also been used to study P450-catalyzed hydroxylation reactions.

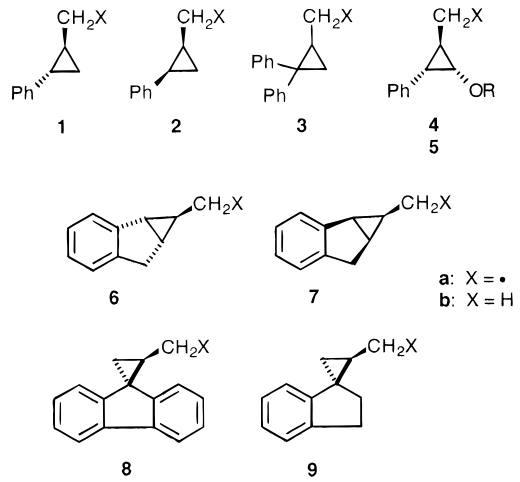
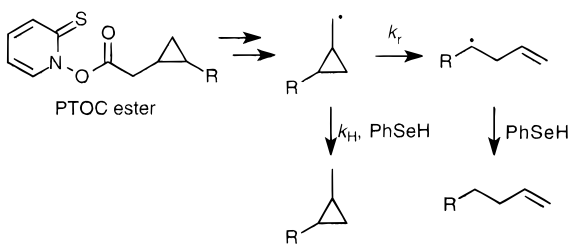


Figure 1. Calibrated phenyl-substituted cyclopropylcarbinyl radical clocks.

Scheme 1



Probes **1b**−**9b** are precursors to primary radicals **1a**−**9a**, which afford primary alkenes upon rearrangement (Scheme 1). A report by Zaks and Dodds[12] in which **1b** was used in a study of the mechanism of CPO-catalyzed hydroxylation reactions combined with the known incompatibility of primary alkenes with CPO[19] prompted us to design probes that yield substituted alkenes upon rearrangement for use in CPO mechanistic studies. To obtain dialkyl- and trialkyl-substituted alkene rearrangement products, alkyl-substituted cyclopropylcarbinyl radical precursors were required. Hence, probes **10b** and **11b** were prepared, and their hydroxylations by CPO[13] and P450[20] and, for probe **10b**, in Gif oxidations[21]

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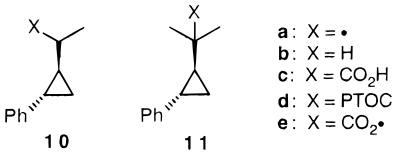
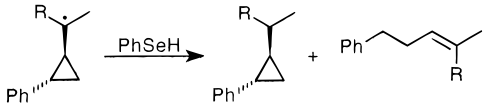
were studied. In this report we present the indirect determinations of the kinetics of the rearrangement of radicals **10a** and **11a** by the PTOC-selenol method (Scheme 1). These secondary and tertiary cyclopropylcarbinyl radicals react nearly as rapidly as their primary radical analogue **1a**.



Results and Discussion

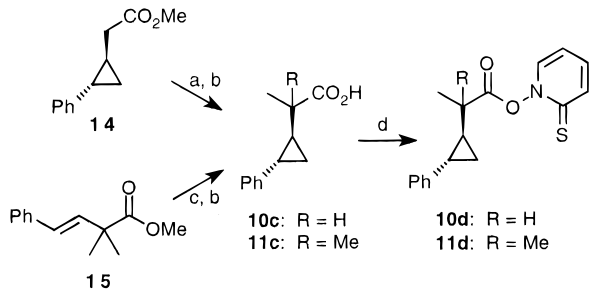
In the PTOC-selenol method, the radical precursors are PTOC[22] esters, a family of carboxylic acid derivatives invented by Barton for synthetic applications.[23] PTOC esters **10d** and **11d** react mainly in radical chain reactions to give acyloxyl radicals (**10e** and **11e**) that rapidly decarboxylate to give the radical of interest (**10a** and **11a**). As shown in Scheme 1, the radical is either trapped by PhSeH or rearranges. The rearranged radical also reacts with the trapping reagent, and the byproduct from the trapping agent (PhSe$^{\cdot}$) reacts with another PTOC ester molecule in a chain propagation step. Because benzeneselenol can be used in high concentrations, it provides the fastest calibrated radical trapping agent available.[5,6] The product mixture is analyzed by GC, and the rate constant for rearrangement is calculated from the product ratio, the rate constant for trapping, and the concentration of the trapping agent.[24]

Precursors and Products. Use of the PTOC-selenol method for calibration of radicals **10a** and **11a** will give the cyclic and acyclic products shown. The preparations of cyclic products **10b** and **11b** were previously reported.[13] Samples of the known acyclic alkene products **12** and **13** were prepared by Wittig reactions according to the methods of Vedejs[25] and Dare,[26] respectively.



The PTOC ester radical precursors **10d** and **11d** were prepared from the corresponding carboxylic acids, **10c** and **11c**, which were synthesized as outlined in Scheme 2. Acid **10c** was prepared in two steps from the known methyl ester **14**.[27] Ester **14** was prepared from the corresponding acetic acid[7] by treatment with diazomethane. This ester was methylated by treating it sequentially with lithium bis(trimethylsilyl)amide (LHMDS) and iodomethane. Saponification of the alkylated product afforded acid **10c** as a mixture of diastereomers

Scheme 2[a]



[a] Key: (a) (i) LHMDS, THF, −78 °C, (ii) MeI, rt. (b) LiOH, MeOH, H_2O. (c) (i) Et_2Zn, CH_2I_2, CH_2Cl_2, −30 °C, (ii) *m*-CPBA, CH_2Cl_2, rt. (d) 2,2′-dipyridyl disulfide bis-*N*-oxide, R_3P, CH_2Cl_2.

in approximately a 3:1 ratio. Because the chiral center at the cyclopropylcarbinyl position is lost in formation of radical **10a**, this mixture was not separated but taken on to a mixture of diastereomers of PTOC ester **10d**. Acid **11c** was prepared in two steps from known ester **15**.[28] Cyclopropanation of **15** with diethylzinc and diiodomethane afforded the cyclopropaneacetate[29] which was saponified to give **11c**. Conversion of **10c** and **11c** to their corresponding PTOC esters **10d** and **11d** was accomplished by the mild 2,2′-dipyridyl disulfide bis-*N*-oxide−tributylphosphine method.[30]

Kinetics of Cyclopropylcarbinyl Radical Ring Openings. PTOC ester precursors **10d** and **11d** were allowed to react in THF in the presence of PhSeH in indirect kinetic studies similar to those previously reported.[7] The reaction mixtures were analyzed by GC to give the results listed in Table 1. Ring opening of the secondary radical **10a** gave both *cis* and *trans* isomers of the alkene product in approximately constant ratios at each temperature. At 25 °C, this ratio was 2.7 which gives a difference in activation free energies for the two nonsymmetric transition states of 0.6 kcal/mol, in good agreement with computations that indicate that the barriers for the two transitions states for ring opening of the 1-cyclopropylethyl radical differ by 0.9 kcal/mol.[31]

The total yields of products were quite high for the tertiary system **11** but generally in the range of 50−60% for the secondary system **10**. In control reactions with alkenes in the presence of PhSeH, we have not observed loss of alkene under the reaction conditions of the kinetic studies, but there exist two interfering processes that can lead to reduced yields of hydrocarbon products.[7] (1) Benzeneselenol can react with the PTOC ester precursor, an activated acylating agent, in a polar reaction, and (2) the first-formed acyloxyl radical can be trapped by PhSeH in competition with the fast decarboxylation step. Because these processes give either a carboxylic acid or an acid derivative, they do not affect the kinetic results other than to reduce the precision by reducing the overall yield of hydrocarbon products. On the basis of the high yields of hydrocarbon products from the tertiary system **11** and the reduced yields in the secondary system **10**, it seems reasonable to conclude that competitive trapping of the

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Table 1. Results of PhSeH Trapping of Radicals 10a and 11a

temp[a] (°C)	$[PhSeH]_m$[b]	R/U[c]	k_r/k_H[d] (M)	% yield[e]
radical **10a**				
25	1.79	40.7	72.9	87
	1.34	47.1	63.1	59
	1.07	56.7	61.6	61
0	1.79	39.8	71.3	56
	0.89	58.4	51.8	50
	0.71	60.0	42.4	49
	0.89	56.2	50.0	66
−21	1.34	27.0	36.2	47
	0.89	38.6	34.3	42
	0.71	70.9	50.1	66
−42	1.07	38.0	40.6	58
	0.89	42.7	37.9	61
	0.62	61.3	37.8	64
radical **11a**				
25	1.84	31.2	57.5	96
	1.58	32.0	50.6	95
	1.31	39.8	52.2	100
0	1.78	27.8	49.5	87
	1.60	31.9	51.0	92
	1.33	36.4	48.4	94
	1.15	39.5	45.4	92
−22	1.33	37.1	50.0	101
	1.15	42.3	48.8	94
	0.97	51.0	49.6	104
−48	1.49	24.0	35.7	99
	1.22	29.5	36.0	102
	1.05	33.6	35.2	98

[a] ±1 °C. [b] Average concentration of PhSeH. [c] Ratio of rearranged to unrearranged hydrocarbon products. [d] Ratio of rate constant for ring opening to that for trapping. [e] Yield of hydrocarbon products determined by GC.

acyloxyl radical in competition with decarboxylation was the major interfering process and that decarboxylation of acyloxyl radical **11e** was faster than that of **10e**.

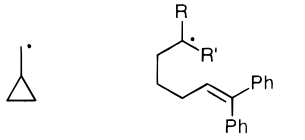
From the ratios of unrearranged to rearranged products and the known concentrations of PhSeH, relative rate constants were calculated from each reaction, and these are listed in Table 1. Relative Arrhenius functions for ring opening and trapping calculated from these values are given in eqs 2 and 3 where k_r is the rate constant for ring opening, k_H is the rate constant for trapping, $\theta = 2.3RT$ in kcal/mol, and errors are at 2σ. For comparison, the relative Arrhenius function for ring opening and PhSeH trapping of the primary radical analogue **1a** is given in eq 1.[7]

$$\text{(for } \mathbf{1a}\text{)}^{7} \quad \log((k_r/k_H)/\text{M}) = (3.07 \pm 0.35) - (1.24 \pm 0.42)/\theta \quad (1)$$

$$\text{(for } \mathbf{10a}\text{)} \quad \log((k_r/k_H)/\text{M}) = (2.63 \pm 0.44) - (1.14 \pm 0.52)/\theta \quad (2)$$

$$\text{(for } \mathbf{11a}\text{)} \quad \log((k_r/k_H)/\text{M}) = (2.24 \pm 0.18) - (0.69 \pm 0.22)/\theta \quad (3)$$

The precisions in the relative Arrhenius parameters in eqs 1−3 are reasonably good, but bimolecular rate constants for reactions of PhSeH with the radicals are necessary for calculating the absolute rate constants for the ring-opening reactions. In the original calibration of radical **1a** and other aryl-substituted primary cyclopropylcarbinyl radicals, the rate constants for the PhSeH trapping reactions employed were those determined by competition against ring opening of the cyclopropylcarbinyl radical (**16**).[6] Recent studies in our laboratory suggest, however, that the rate constants for ring openings of **16** used in those calculations and the resulting rate constants for PhSeH reactions are too large, and the suggestion was made that the "top end" of the alkyl radical kinetic scale should be reduced.[32] At ambient temperatures, the reductions in rate constants would amount to about 30−40% of the values.



16 **17**: R = R' = H
18: R = Me, R' = H
19: R = R' = Me

In the recent study, we found that radicals **17**−**19** reacted with PhSeH with nearly the same rate constants.[32] Therefore, we assume that the aryl-substituted cyclopropylcarbinyl radicals will react with PhSeH with rate constants equal to those of the appropriate analogue among radicals **17**−**19**. Using the absolute Arrhenius functions for PhSeH reactions determined in that work,[32] the absolute Arrhenius functions for ring openings of radicals **1a**, **10a**, and **11a** are given in eqs 4−6 where errors have been propagated at 2σ. These functions give rate constants for ring opening at 20 °C of 1.6×10^{11} s^{-1} (**1a**), 7×10^{10} s^{-1} (**10a**), and 7×10^{10} s^{-1} (**11a**). Note that the values for the rate constants for ring opening of **1a** are smaller than those previously reported[7] due to the adjustment of the PhSeH trapping kinetics.

$$\text{(for } \mathbf{1a}\text{)}^{7} \quad \log(k_r/s^{-1}) = (13.80 \pm 0.38) - (3.46 \pm 0.46)/\theta \quad (4)$$

$$\text{(for } \mathbf{10a}\text{)} \quad \log(k_r/s^{-1}) = (12.52 \pm 0.48) - (2.28 \pm 0.57)/\theta \quad (5)$$

$$\text{(for } \mathbf{11a}\text{)} \quad \log(k_r/s^{-1}) = (12.21 \pm 0.38) - (1.85 \pm 0.50)/\theta \quad (6)$$

Due to the magnitude of the errors in the parameters in eqs 4−6, one probably should not attempt to interpret differences in the apparent enthalpies and entropies of activation of the ring-opening reactions. In addition, we caution that the rate constants calculated from eqs 4−6 are likely to be increasingly in error as one moves farther from ambient temperatures. For temperatures more than 25 °C above ambient, the calculated rate constants will be extrapolated from the temperature range studied here and in the calibrations of PhSeH.[32] At temperatures below ambient, the calculated rate constants are likely to incorporate larger accumulated errors that result in part from the fact that the PhSeH trapping reactions are partially diffusion controlled.[32]

Nevertheless, we believe the rate constants for ring openings of these radicals at ambient temperatures are reasonably accurate in an absolute sense and quite accurate in a relative sense. The accuracy is indicated in a comparison of the rate constants for ring opening of the three series of 1°, 2°, and 3° cyclopropylcarbinyl radicals shown in Figure 2 where relative rate constants

(32) Newcomb, M.; Choi, S.-Y.; Horner, J. H. Submitted for publication.

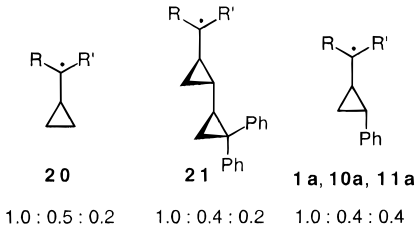


Figure 2. Relative rate constants at 20 °C for ring openings of 1°, 2°, and 3° radicals for each series.

at 20 °C are given. The data for radicals **20** is from a variety of indirect kinetic studies,[2,4,33] and those for radicals **21** were obtained by direct LFP measurements.[31] Good internal consistency of the relative rate constants for these series is found even though radicals **1a**, **10a**, and **11a** ring open 3 orders of magnitude faster than radicals **20** and **21**. The consistent trends appear to be in line with computational results that indicate that electronic effects of methyl substitution in the secondary alkyl radical **20** (R = Me, R′ = H) are minor in comparison to steric effects.[34]

Experimental Section

General Methods. Commercially available reagents were used as received. All moisture sensitive reactions were carried out in flame-dried glassware under a nitrogen atmosphere. THF was distilled under a nitrogen atmosphere from sodium and benzophenone ketyl. Methylene chloride was distilled under a nitrogen atmosphere from phosphorus pentoxide.

NMR spectra were acquired at 300 and 75 MHz for ^{1}H and ^{13}C, respectively. Gas chromatographic analyses were performed using flame ionization detection with 15 m × 0.54 mm bonded phase SE-54 and Carbowax columns. Gas chromatography/mass spectral (GC/MS) analyses were performed using a Hewlett-Packard model 5890 GC interfaced to a Hewlett-Packard model 5971 mass selective detector (30 m × 0.25 mm capillary bonded phase Carbowax column, Alltech). High-resolution mass spectral analyses were performed by the Central Instrumentation Facility at Wayne State University (Detroit, MI). Melting points are uncorrected. Radial chromatography was performed on plates coated with TLC grade silica gel with gypsum binder and fluorescent indicator.

2-(*trans*-2-Phenylcyclopropyl)propionic Acid (10c). A solution of methyl (*trans*-2-phenylcyclopropyl)acetate[27] (**14**) (1.30 g, 6.83 mmol) in THF (50 mL) under a nitrogen atmosphere was cooled to −78 °C. To this was added a solution of LHMDS (1.0 M in THF, 7.0 mL, 7.00 mmol). After 15 min, iodomethane (1.3 mL, 20.2 mmol) was added. The mixture was allowed to warm gradually to room temperature, and after 16 h, the reaction mixture was poured into a saturated, aqueous NH_4Cl solution (100 mL) and extracted with ether (3 × 50 mL). The combined organic phase was washed with water (75 mL) and brine (75 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was chromatographed on silica gel (10% ethyl acetate in hexanes) to afford a mixture of diastereomers, inseparable by GC, of methyl 2-(*trans*-2-phenylcyclopropyl)-propionate (0.58 g, 2.84 mmol, 42%) as a clear, colorless oil. Reduction of the inseparable mixture of esters with LAH afforded a mixture of diastereomeric alcohols in a 3:1 ratio as determined by GC. GC/mass spectral analysis of the mixture showed that both isomers had (M^+) at m/z = 176.

Hydrolysis of a mixture of diastereomers of the above ester (180 mg, 0.882 mmol) with $LiOH·H_2O$ (185 mg, 4.41 mmol) in methanol (9 mL) and H_2O (3 mL) at room temperature gave the corresponding acid **10c** (161 mg, 96%) as a mixture of diastereomers. The NMR spectra are superimpositions of those of the two diastereomers in an approximately 3:1 ratio. Spectra for the major diastereomer follow. ^{1}H NMR ($CDCl_3$): δ 0.80−0.88 (1H, dt, J_1 = 8.4 Hz, J_2 = 5.4 Hz), 0.93−1.09 (1H, m), 1.15−1.30 (1H, m), 1.30−1.35 (3H, m), 1.95−2.06 (1H, m), 2.30−2.52 (1H, m), 7.08−7.29 (5H, m), 11.2−11.8 (1H, bs). ^{13}C NMR ($CDCl_3$): δ 14.0, 16.1, 22.4, 25.6, 43.9, 125.6, 126.2, 128.2, 142.3, 181.6.

1-[[[(*trans*-2-Phenylcyclopropyl)ethyl]carbonyl]oxy]-2(1*H*)-pyridinethione (10d). To a solution of acid **10c** (160 mg, 0.842 mmol) and 2,2′-dipyridyl disulfide bis-*N*-oxide (1.1 equiv, 234 mg, 0.93 mmol) in dry CH_2Cl_2 (10 mL) in a flame-dried flask wrapped with aluminum foil was added Ph_3P (1.1 equiv, 244 mg, 0.93 mmol) at room temperature under nitrogen. The reaction mixture was stirred for 3 h and then treated with 10 mL of a 10% aqueous Na_2CO_3 solution. The organic layer was separated, and the aqueous layer was extracted with 10 mL of CH_2Cl_2. The combined organic extracts were washed with a saturated aqueous NaCl solution (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (hexanes/EtOAc, 7/3, v/v) under subdued light gave PTOC ester **10d** (170 mg, 0.57 mmol, 67.7%) as a mixture of diastereomers. The NMR spectra are superimpositions of those of the two diastereomers in an approximately 3:1 ratio. Spectra for the major diastereomer follow. ^{1}H NMR ($CDCl_3$): δ 0.95 (1H, m), 1.12 (1H, m), 1.36−1.48 (1H, m), 1.52 (3H, d, J = 7.2 Hz), 2.10−2.12 (1H, m), 2.36−2.48 (1H, m), 6.55−6.60 (1H, dt, J_1 = 6.9 Hz, J_2 = 1.8 Hz), 7.08−7.30 (6H, m), 7.42−7.45 (0.7H, dd, J_1 = 7.2 Hz, J_2 = 1.5 Hz), 7.66−7.69 (1H, J_1 = 6.9 Hz, J_2 = 1.8 Hz). ^{13}C NMR ($CDCl_3$): δ 14.4, 16.3, 22.7, 25.5, 42.4, 112.5, 125.8, 125.9, 128.3, 133.4, 137.4, 137.5, 141.7, 171.1, 175.7.

2-Methyl-2-(*trans*-2-phenylcyclopropyl)propionic Acid (11c). To a solution of **15**[28] (2.55 g, 12.5 mmol) and diethylzinc (75.0 mL, 1.0 M in hexanes, 75.0 mmol) in CH_2Cl_2 (200 mL) at −20 °C under a nitrogen atmosphere was added CH_2I_2 (12.1 mL, 150.2 mmol) slowly via syringe. The mixture was allowed to warm to room temperature gradually, and after a total of 16 h, the suspension was poured into a saturated aqueous NH_4Cl solution (300 mL). The mixture was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic layers were washed with water (200 mL) and brine (200 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was dissolved in CH_2Cl_2 (100 mL), and 3-chloroperoxybenzoic acid (2.16 g, 12.5 mmol) was added. The mixture was stirred for 8 h at room temperature and then diluted with additional CH_2Cl_2 (200 mL). The mixture was washed with saturated aqueous $NaHCO_3$ (200 mL), water (200 mL), and brine (200 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was chromatographed on silica gel (10% ethyl acetate in hexanes) to afford the cyclopropyl ester (1.41 g, 6.46 mmol, 52%) as a clear, colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.87 (1H, dt, J_1 = 8.7 Hz, J_2 = 5.4 Hz), 0.94−1.01 (1H, m), 1.17 (3H, s), 1.18 (3H, s), 1.33−1.39 (1H, m), 1.90 (1H, dt, J_1 = 9.3 Hz, J_2 = 5.4 Hz), 3.69 (3H, s), 7.07−7.17 (3H, m), 7.22−7.29 (2H, m). ^{13}C NMR ($CDCl_3$): δ 11.3, 19.1, 23.2, 23.4, 31.0, 41.7, 51.8, 125.5, 126.2 (2C), 128.2 (2C), 142.9, 177.8. HRMS: calcd for $C_{14}H_{18}O_2$, 218.1307; found, 218.1304.

A solution of the above ester (0.32 g, 1.47 mmol) and $LiOH·H_2O$ (0.62 g, 14.7 mmol) in water (5 mL) and methanol (20 mL) was stirred at room temperature for 6 h. The solvents were removed in vacuo, and the resulting white solid was dissolved in water (25 mL). This solution was made acidic (concentrated HCl) and then extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to afford **11c** (0.25 g, 1.22 mmol, 83%) as a white solid. Mp: 60−61 °C. ^{1}H NMR ($CDCl_3$): δ 0.94 (1H, dt, J_1 = 9.0 Hz, J_2 = 5.4 Hz), 1.04−1.11 (1H, m), 1.23 (3H, s), 1.26 (3H, s), 1.44−1.50 (1H, m), 1.99 (1H, dt, J_1 = 9.0 Hz, J_2 = 5.1 Hz), 7.14−7.34 (5H, m), 11.95 (1H, bs). ^{13}C NMR ($CDCl_3$): δ 11.5, 19.2, 22.8, 23.3, 30.7, 41.6, 125.6, 126.2 (2C), 128.3 (2C), 142.8, 184.5. HRMS: calcd for $C_{13}H_{16}O_2$, 204.1150; found, 204.1155.

1-[[[1-Methyl(*trans*-2-phenylcyclopropyl)ethyl]carbonyl]-oxy]-2-(1*H*)-pyridinethione (11d). To a solution of acid **11c** (220 mg, 1.08 mmol) and 2,2′-dipyridyl disulfide bis-*N*-oxide (1.1 equiv, 299 mg, 1.19 mmol) in dry CH_2Cl_2 (10 mL) in a flame-

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dried flask wrapped with aluminum foil was added *n*-Bu_3P (1.1 equiv, 294 μL, 1.19 mmol) at 0 °C under nitrogen. After 2 min, the ice bath was removed. The reaction mixture was stirred for 40 min before 10% aqueous Na_2CO_3 (10 mL) was added. The organic layer was separated, and the aqueous layer was extracted with 10 mL of CH_2Cl_2. The combined organic extracts were washed with a saturated NaCl solution (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (hexanes/EtOAc, 7/3, v/v) under subdued light gave PTOC ester **11d** (220 mg, 0.70 mmol, 64.8%). ^{1}H NMR ($CDCl_3$): δ 1.01 (1H, dt, $J_1 = 8.7$ Hz, $J_2 = 5.7$ Hz), 1.15 (1H, dt, $J_1 = 9.3$ Hz, $J_2 = 6.0$ Hz), 1.40 (3H, s), 1.43 (3H, s), 1.55−1.62 (1H, m), 2.01−2.08 (1H, m), 6.53−6.58 (1H, dt, $J_1 = 6.9$ Hz, $J_2 = 1.8$ Hz), 7.11−7.19 (4H, m), 7.24−7.27 (2H, m), 7.33−7.36 (1H, dd, $J_1 = 6.9$ Hz, $J_2 = 1.5$ Hz), 7.63−7.67 (1H, dd, $J_1 = 8.7$ Hz, $J_2 = 1.8$ Hz). ^{13}C NMR ($CDCl_3$): δ 11.5, 19.3, 22.7, 23.2, 30.5, 41.9, 112.5, 125.8, 126.0, 128.3, 133.2, 137.5, 142.0, 172.7, 175.9.

Indirect Kinetics. Benzeneselenol, prepared by the method of Foster,[35] was distilled under subdued light. Samples were divided into 1-mL portions and sealed under vacuum in ampules that were stored at ca. −70 °C. The amount of diphenyl diselenide contaminant (typically <4%) in each sample of PhSeH was determined by GC prior to use. The indirect method used was similar to those previously reported.[7] A flame-dried tube shielded from light containing a small stir bar, a mixture of radical precursor (0.04−0.05 M), PhSeH, and a hydrocarbon standard (dodecane or octane) in freshly distilled THF was sparged with nitrogen. The tubes were equilibrated in a temperature-regulated bath for several minutes. The shields were removed, and the stirring mixture was irradiated with a 150-W tungsten filament lamp placed 0.4 m from the tube. After 40 min, the tubes were cooled at −78 °C and analyzed by GC. All yields reported for indirect kinetic experiments were calculated from response factors determined with authentic samples.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **10c**, **10d**, **11c**, and **11d** (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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